California Environmental Protection Agency

Air Resources Board

Draft

Protocol for the Application and Ambient Air Monitoring for Acephate and Methamidophos In Fresno County During Summer, 2002

Quality Management Branch
Monitoring and Laboratory Division

Project No.
P-02-003

Date: July 17, 2002

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This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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I. Introduction

At the request (January 2, 2002, Memorandum, Helliker to Lloyd) of the California Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) staff will determine airborne concentrations of the pesticides acephate and methamidophos in Fresno County over a seven week ambient monitoring program and over three day application monitoring programs. This monitoring will be done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB to "...document the level of airborne emissions ... of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. The ambient monitoring will be conducted for seven consecutive weeks between July 8 and August 23, 2002 to coincide with the use of these two organophosphate chemicals as insecticides. California growers use acephate and methamidophos to control a variety of plant and soil insects.

The sampling and analysis for acephate and methamidophos will follow the procedures and quality assurance guidelines described in the "Quality Assurance Plan for Pesticide Air Monitoring" (May 11, 1999 version) included as Attachment I as well as the procedures described in the "Standard Operating Procedure for the Sampling and Analysis of Methamidophos and Acephate in Ambient and Application Air Monitoring using Gas Chromatography with a Nitrogen-Phosphorous Detector and a Flame Photometric Detector" (Attachment II) and the pesticide adsorbent tube sampling procedures outlined in Attachments IV and V.

II. Sampling

Samples will be collected by passing a measured volume of ambient air through XAD-2 resin. The sampling manifold is shown in Figure 1. The exposed XAD-2 resin tubes (SKC #226-30-06) are stored in an ice chest (on dry ice) or in a freezer until desorbed with organic solvent. The tubes are 8 mm x 110 mm with 400 mg XAD-2 in the primary section and 200 mg in the secondary section. The flow rate of 3.0 standard liters per minute (slpm) will be accurately measured and the sampling system operated continuously for 24 hours (ambient) with the exact operating interval recorded in the log book. The tubes will be protected from direct sunlight and supported about 1.5 meters above the ground during application monitoring sampling periods and 1.5 meters above roof tops for the ambient monitoring. At the end of each sampling period, the tubes will be placed in culture tubes with an identification label affixed. Subsequent to sampling, the sample tubes will be transported on dry ice, as soon as reasonably possible, to the

ARB Monitoring and Laboratory Division laboratory for analysis. The samples will be stored in the freezer or extracted/analyzed immediately.

Each sample train consists of an adsorbent tube, Teflon fittings and tubing, rain/sun shield, rotameter (or needle valve), train support, and either a 12 volt DC or a 115 volt AC vacuum pump. Tubes are prepared for use by breaking off the sealed glass ends and immediately inserting the tube into the Teflon fitting. The tubes are oriented in the sample train according to a small arrow printed on the side indicating the direction of flow. A needle valve with a range of 0-5 slpm is used to control sample flow rate. The flow rates will be set using a calibrated digital mass flow meter (MFM), scaled from 0-5 slpm, before the start of each sampling period. The flow rate is also checked and recorded, using the MFM, at the end of each sampling period. Samplers will be leak checked prior to each sampling period, with the sampling tubes installed. Any change in flow rates will be recorded on the field log sheet. The pesticide sampling procedures for adsorbent tubes are included as Attachment IV (ambient) and V (application).

Ambient Monitoring

The DPR recommendations for acephate and methamidophos request that ambient monitoring occur in Fresno County for 7 consecutive weeks between July 8 and August 23, 2002. Four sampling sites will be selected in relatively high-population areas or in areas frequented by people (e.g., schools or school district offices, fire stations, or other public buildings). At each site, 28 discrete 24-hour samples will be collected, Monday through Friday (4 samples/week), during the 7-week sampling period. Background samples will be collected at the ARB air monitoring site in Fresno. Collocated (replicate) samples will be collected for six days (each Wednesday) at each sampling location.

The sites will be selected by ARB personnel based on the historical use of acephate and methamidophos in Fresno County. Sites will be selected for their proximity to these areas with considerations for both accessibility and security of the sampling equipment. ARB understands that DPR staff will verify and quantify the actual use of chlorothalonil that takes place during the study when the information becomes available.

Application Monitoring

The use patterns for acephate and methamidophos suggest that application-site monitoring may be conducted in Fresno County sometime during the ambient study, and that the monitoring be associated with an application of each compound at the highest use rate of approximately 1.0 pounds active ingredient (AI) per acre. As methamidophos is a breakdown product of acephate, both acephate and methamidophos will be monitored during the acephate application study. A separate study for methamidophos only will also be conducted.

The exact application monitoring schedules will vary based on the type and length of

application but will follow the schedule guidelines outlined below in Table 1. Ideally, each monitoring study will include samples taken before, during, and for approximately 72 hours following application.

TABLE 1. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

Sample period begins:	**Sample duration time**
Background (pre-application)	24 hours
During application	Length of application time
End of application	1 hour (or up to 1 hour before sunset)[1]
1 hour post-application	2 hours (or up to 1 hour before sunset)[1]
3 hour post-application	3 hours (or up to 1 hour before sunset)[1]
6 hour post-application	6 hours (or up to 1 hour before sunset)[1]
1 hour before sunset	Overnight[2] (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	24-hour (until 1 hour after sunrise)

[1] These sample duration times will be adjusted depending on length of application and time of sunset.
[2] All overnight samples must include the period from one hour before sunset to one hour after sunrise. If the application extends beyond "1 hour before sunset" then the overnight sample will be started at the end of application.

Occasionally, a pesticide application may occur over the course of two or more days. In these instances, samples are collected during the first daily application followed by a sample from the end of application to 1 hour before sunset (if applicable). An overnight sample is then collected which will end at either the start of application or 1 hour after sunrise the next morning, whichever is first (same for third or more application days). If the day-2 application does not start on or before '1 hour after sunrise' and the expected time between '1 hour after sunrise' and the start of application is more than 2 hours, then an additional sample will be collected during this period. Following the end of the final application, samples are collected according to the above schedule, starting with the 1-hour sample. As stated above, if the application extends beyond "1 hour before sunset" then the overnight sample will be started at the end of application (i.e., no 1, 2, or 3 hour samples will be collected post application in this case).

A minimum of eight samplers will be positioned, one on each side of the field and one in each corner. A ninth sampler will be collocated at one position (downwind). Background (before application) samples should be collected for 24 hours. Ideally, samplers should be placed at 20 meters from the field. Conditions at the site will dictate the actual placement of monitoring stations.

The exact location of the application monitoring studies have not yet been determined. ARB

staff will contact the County Agricultural Commissioner's offices in the Fresno County area to coordinate the selection of study sites and the test dates. The County Agricultural Commissioner's staff will make initial contact with, or will at least provide a list of local contacts for growers, applicators, and/or pesticide control advisers that may be willing to cooperate in conducting the study. Monitoring sites are arranged with the voluntary cooperation of growers and applicators. ARB staff will investigate contacts until a cooperative grower is found and an appropriate site is selected. Permission to conduct the study will be obtained from the application plot land-owner and owners of adjacent land where samplers will be positioned.

Candidate fields for application monitoring will be 10 acres or larger. The crop type or specific application method for the application study were not specified by the DPR. However, the DPR recommended that, "...monitoring should occur at a site using the highest allowed use rates (i.e., 1 pound AI per acre for acephate and methamidophos...)".

ARB will provide the following information in the monitoring report:

1) An accurate record of the positions of the monitoring equipment with respect to the field, including the exact distance that the sampler is positioned from the field,
2) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, etc.,
3) meteorological data collected at a minimum of 15 minute intervals including wind speed and direction, humidity, and comments regarding degree of cloud cover,
4) the elevation of each sampling station with respect to the field, and
5) the orientation of the field with respect to North (identified as either true or magnetic north).
6) The start and end time of the application each day.

III. Analysis

The draft "Standard Operating Procedure for the Sampling and Analysis of Methamidophos and Acephate in Ambient and Application Air Monitoring using Gas Chromatography with a Nitrogen-Phosphorous Detector and a Flame Photometric Detector" (June 6, 2002, draft version) is included as Attachment II. The results of method validation studies are included as Attachment III. The procedures consist of extraction of the exposed XAD-2 resin with an organic solvent followed by GC analysis. The DPR requested target 24-hour estimated quantitation limits (EQL) of 5.0 ng/m^3 and 1.0 ng/m^3 for acephate and methamidophos for the ambient study and target EQLs of 100 ng/m^3 and 50 ng/m^3 for acephate and methamidophos for the application studies. The EQLs actually achieved by the method were 17.3 ng/m^3 and 6.12 ng/m^3 for acephate and methamidophos respectively.

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IV. Quality Assurance

Field Quality Control for the ambient monitoring will include:

1) Four field spikes collected under the same environmental and experimental conditions as those occurring at the time of ambient sampling. The field spikes will be obtained by sampling ambient air at the urban background monitoring site (ARB Fresno site) for 24-hour periods at 3.0 slpm (i.e., collocated with an ambient sample). One field spike each will be collected during weeks 1, 3, 4 and 6.

2) Four trip spikes prepared at the same level as the field spikes.

3) Four lab spikes prepared at the same level as the field and trip spikes.

4) Collocated (replicate) samples will be taken for six days (each Wednesday) at each sampling location.

5) A trip blank will be obtained each week of sampling.

Field Quality Control for the application monitoring will include:

1) Four field spikes collected under the same environmental and experimental conditions as those occurring at the time of ambient sampling. The field spikes will be obtained by sampling ambient air during background monitoring at the application site for the same duration as the background samples at 3.0 slpm (i.e., collocated with background samples).

2) Four trip spikes prepared at the same level as the field spikes.

3) Four lab spikes prepared at the same level as the field and trip spikes.

4) Collocated (replicate) samples will be taken for all samples at one of the sampling locations (downwind).

5) One trip blank will be obtained during the study.

A chain of custody sheet will accompany all samples. Mass flow meters will be calibrated by the ARB Standards Laboratory. The flow rate of each sampler will be audited by the ARB Quality Assurance Section prior to the monitoring studies.

V. Sample Labeling

Samples for the application study will be labeled using the following format:

Location-Chemical-Sampling Period-Type of Sample

Where:
Location is designated as north 1, 2 or 3 (N1, N2, N3), west (W), south 1, 2 or 3 (S1, S2, S3), and east (E). These designations can be revised as necessary depending on the configuration of the field.

Acephate is designated as A; Methamidophos is designated as M.

Sampling period is designated as B (for background) or 1 through 9 (# of periods can vary).

The type of sample is designated as S (sample), CO (collocated), TB (trip blank), TS (trip spike), and FS (field spike).

Examples:	S2-A-B-S	(South2, Acephate, background, sample)
	S2-A-B-FS	(South2, Acephate, background, field spike)
	S2-A-1-S	(South2, Acephate, sampling period 1, sample)
	S2-A-1-CO	(South2, Acephate, sampling period 1,collocated)

Samples for the ambient study will be labeled using the following format:

Location-Chemical-Sampling Period-Type of Sample

Where:
Location is designated by 3-letters. The designations will be defined after the sites have been chosen.

Acephate/Methamidophos is designated as AM.

Sampling period is designated as 1 through 28 (e.g., 24 periods in 6 weeks).

The type of sample is designated as S (sample), CO (collocated), TB (trip blank), TS (trip spike), and FS (field spike).

Example: ARB-AM-1-S (ARB Fresno site, Acephate/Metham., period 1, sample)
ARB-AM-1-CO (ARB Fresno site, Aceph/Metham., period 1, colloc.)

VI. Personnel

ARB personnel involved with coordinating and conducting the field activities will consist

of staff of the Air Quality Surveillance Branch, ARB.

VII. Safety Recommendations

The DPR's "Use Information and Air Monitoring Recommendations for the Pesticide Active Ingredients Acephate, Chlorothalonil, and Methamidophos" (February 21, 2002 memo, Sanders to Cook) include the following safety recommendations.

Acephate:

"The acephate product labels warn that acephate may be harmful if swallowed and cause eye irritation. Applicators should avoid breathing dust or spray mist and wash hands thoroughly after handling. Children and pets should not come into treated areas until the sprays have dried."

"According to the product labels, proper protective equipment (PPE) for applicators, handlers, mixers, and loaders include long-sleeve shirt and long pants, waterproof gloves, footwear plus socks, and chemical resistant headgear (for overhead exposure). PPE is also required for early entry (restricted-entry interval of 24 hours) to treated areas where contact may occur with anything that has been treated. Monitoring personnel should prevent exposure to the spray mist and treated plants, soil, or water and should refer to the label of the actual product used for further precautions."

Methamidophos:

"The methamidophos product labels warn that methamidophos is hazardous to humans and domestic animals. It is fatal if swallowed, inhaled, or absorbed through the skin. The label warns not to breathe vapor or mist and that the product is rapidly absorbed through the skin."

"Monitoring personnel should use proper protective equipment to prevent exposure to the vapors or spray mist and refer to the label of the actual product used for further precautions. According to the product labels, PPE for applicators and other handlers include coveralls over short sleeve shirt and short pants, chemical resistant gloves $\geq$ 14 mils, chemical resistant footwear plus socks, protective eyewear, chemical resistant headgear (for overhead exposure), a chemical resistant apron when cleaning, mixing, or loading, and a respirator with an organic-vapor removing cartridge with a pre-filter for pesticides or a canister approved for pesticides or a NIOSH approved respirator with an organic vapor cartridge with any N, R, P, or HE pre-filter. The restricted-entry interval (REI) is 48 hours, the REI is increased to 72 hours in outdoor areas where rainfall is less than 25 inches per year."

Attachment III

Method Validation Results

Air Resources Board

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Winston H. Hickox
Agency Secretary

Gray Davis
Governor

MEMORANDUM

TO: Webster Tasat, Manager
Operations Planning and Assessment Section

FROM: Russell Grace, Manager //s//
Special Analysis Section

DATE: October 30, 2002

SUBJECT: METHOD VALIDATION DATA FOR ANALYSIS OF METHAMIDOPHOS AND ACEPHATE

The Special Analysis Section provides laboratory support for the pesticide air monitoring program implemented by the ARB at the request of the Department of Pesticide Regulation. One of the responsibilities of the SAS is laboratory analytical method development. By way of this memo, we are providing you with the method validation data generated in the development of the methamidophos and acephate analytical method for the 2002 monitoring season. The attached tables contain the currently available data generated to determine the method detection limit (MDL), estimated quantitation limit (EQL), reproducibility, collection and extraction efficiency, storage stability and breakthrough.

All of the method development procedures were summarized in the draft standard operating procedure (SOP) for methamidophos and acephate. This draft SOP was previously provided to you.

If you have any questions, please contact T.E. Houston, Ph.D., at 322-2365 or me at 322-0223.

Attachment
cc: Michael Poore
T.E. Houston
Jim Omand
Michael Orbanosky
Kevin Mongar

TABLE 1
METHOD DETECTION LIMIT
Methamidophos and Acephate 2002

Date:07/02/02 XAD spikes Sample	**Methamidophos** (spike: 5 ng/ml) Amount Quantitated	**Acephate** (spike: 15 ng/ml) Amount Quantitated
1	5.040	25.530
2	4.840	26.080
3	5.030	24.590
4	4.310	23.760
5	4.080	23.400
6	5.060	23.820
7	4.620	25.230
Average	4.711	24.630
Standard Deviation (sd)	0.391	1.017
MDL=3.14*sd	1.227	3.192
EQL=5*MDL	6.133	15.960

TABLE 2
INSTRUMENT REPRODUCIBILITY

Methamidophos		Acephate	
Standard	**Amount: ng/ml**	**Standard**	**Amount: ng/ml**
5 ng/ml	5.83	15 ng/ml	17.69
	5.40		16.94
	5.80		17.10
	5.36		15.96
	5.32		15.21
Average	5.54	Average	16.58
Standard Dev.	0.25	Standard Dev.	0.99
40 ng/ml	36.3	80 ng/ml	68.4
	37.4		74.1
	37.8		72.9
	36.9		71.8
	36.4		69.2
Average	37.0	Average	71.3
Standard Dev.	0.64	Standard Dev.	2.42
100 ng/ml	96.8	150 ng/ml	146.9
	97.9		152.8
	94.8		146.1
	95.4		143.5
	98.6		146.3
Average	96.7	Average	147.1
Standard Dev.	1.61	Standard Dev.	3.43

TABLE 3
COLLECTION AND EXTRACTION EFFICIENCY

	Methamidophos	Acephate
Low spikes:	5 ng/ml	15 ng/ml
	116.5 % +/- 12.4	193.0 % +/- 29.6
High spikes:	70 ng/ml	100 ng/ml
	46.4 % +/- 2.1	110.9 % +/- 7.4

TABLE 4
STORAGE STABILITY STUDY

Day	% Recovery Methamidophos low	high	% Recovery Acephate low	high
0	86.6+/- 8.7	98.3 +/- 1.0	148.2 +/- 16	111.5 +/- 1.0
8	133.1 +/- 11	89.4 +/- 2.9	148.0 +/-11.7	118.3 +/- 2.7
14	105.0 +/- 21.9	76.5 +/- 10.6	146.4 +/- 10.3	80.7 +/- 8.0
21	95.2 +/- 7.3	94.1 +/- 3.2	153.2 +/- 5.5	126.5 +/- 7.7

TABLE 5
BREAKTHROUGH STUDY

Date: 09/27/02 XAD-2 Spike (500 ng/ml) Run at 3LPM for 24 hrs	Methamidophos		Acephate	
	ng/ml	% recovery	ng/ml	% recovery
XAD Blank	<MDL		<MDL	
XAD Lab Spike	485.2	97.04	559.3	111.86
Field Spike	441.85	88.37	744.7	148.94
Front Bed	391.6	78.32	675.7	135.14
	330	66.0	753.5	150.70
Average	387.82	77.56	724.63	144.93
Standard Deviation	56.02	11.20	42.61	8.52
Back Bed	<MDL		<MDL	

Attachment IV

Pesticide Sampling Procedures for Adsorbent Tubes
For Ambient Monitoring Studies

Pesticide Ambient Sampling Procedures
For Adsorbent Tubes

Overview:

-Collect samples over the six week sampling period; 24 hour samples; Four sampling periods per week per site; Five sampling sites plus an urban background site (ARB Fresno station).

-Collect a collocated sample from each site each Wednesday,

-Submit 1 trip blank per week,

-With the trip blank there normally will be 31 samples collected per week,

-4 field spikes will be run at the ARB site (time collocated exactly with the ambient sample. The field spikes will be distributed over the monitoring period (e.g., 1 per week on weeks 1, 3, 4, and 6). A trip spike will also accompany each field spike. These field and trip spikes will be logged in and shipped along with the regular samples. The field and trip spikes will be kept on dry ice during transport to and storage in the field.

-All samples are stored either in an ice-chest on dry ice or in a freezer,

-The field log sheet is filled out as the sampling is conducted. The originals stay in the field binder. Please include a copy with sample shipments. All QA samples must be logged onto the log sheet,

-The chain of custody (COC) forms are filled out prior to sample shipment; the originals are shipped with the samples; make and retain copies if desired (not necessary),

-(Disregard if samples are driven back to Sacramento) The samples are shipped by UPS, next day delivery, to 13th and T. This is normally done each Monday. The original chain of custody sheets must accompany the samples. The samples are shipped on 5 pounds of dry ice. Review the COCs and log sheet to insure that all documentation is correct and that the appropriate QA samples have been included.

Sampling Procedure:

Materials that will be needed on the roof to conduct the sampling include:

- -Clip board with log sheets
- -pencils/pens
- -sample labels
- -sample cartridges
- -end caps
- -plastic test tubes
- -0 to 5 slpm mass flow meter (MFM) with battery

Figure out your route for sampling the six locations and try to keep this the same throughout

the study. In general, try to make each sampling period 24 hours; e.g., if start time is 11:10 then end time should be 11:10. (round off to the nearest 5 minutes.) The sample period may not always be exactly 24 hours; but that is the target time frame.

Preparation and Set-up

On the way to the first site, plug the MFMs into the batteries. It takes the MFMs about 10 minutes to warm up before they can be used. Leave the MFMs plugged in until the last sample for the day is taken; then unplug for the night to minimize drop in battery charge. Recharge the batteries once per week to be on the safe side.

Upon arrival at the site, check in if needed. Fill out the sample labels for that site. I suggest a backpack and/or fannypacks to carry the stuff to the roof.

Securely attach one adsorbent sample cartridge to the sampling tree. MAKE SURE THE ARROW ON THE CARTRIDGE IS POINTING TOWARDS THE SAMPLE LINE.

Perform the leak check on each sample line by placing a plastic tube cap over the inlet of the cartridge (with the pump on). The rotameter ball should fall to zero. The leak check should be performed before setting the flows with the MFMs.

Using the 5 slpm MFM set the flow rate exactly to 3.0 slpm.

Make sure that the rain/sun cover is pulled down over the sample tube.

Fill out the log sheet, including: log #, start date, time, start counter reading, leak check OK, any comments and the weather conditions.

Sample collection and Shipment

Measure (do not re-set) the flow rates at the end of the sampling period with the MFMs; leak check the sample lines; record the end data on the log sheet.

Remove the sample cartridge and cap the ends. Attach the sample label like a flag on the secondary end of the tube. Make sure that the label does not cover the glass wool separating the primary and secondary beds in the cartridge.

Place the cartridge in the plastic test tube shipping container.

Place all the samples for each day (6) in a zip-lock bag and place on dry ice in a cooler or in a freezer. While driving the route the collected samples need to be kept on dry ice.

Collect the collocated (duplicate) samples from each site every Wednesday. These should be started and stopped at the same times as the regular samples.

Collect a trip blank (TB) once per week,while at one of the field sites. It doesn't matter

which site (or which day) but note it in the comment section of the log sheet. The TB is collected by breaking the ends off of a tube, capping and labeling as usual and storing along with the rest of the samples. Log the TB into the log sheet.